Effect of the Inherent Structure of Rh Nanocrystals on the Hydriding Behavior under Pressure

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ABSTRACT: Tailoring the inherent structure of materials is an effective way to improve the hydrogen storage capacity of metal materials. In this work, we report the effect of rhodium (Rh) nanocrystals (NCs) on the hydrogenation reaction. We found that Rh NCs could form rhodium monohydride (RhH) at a lower pressure than the bulk Rh because of its high specific surface area and structure defects. In addition, Rh NCs in the form of icosahedrons exhibited a much higher hydrogen absorption efficiency than Rh nanocubes. Furthermore, much smaller irregular Rh nanoparticles are even partially converted to RhH at lower pressure because of the nanosize effect. We thus believe that it is possible to design materials with excellent hydrogen storage properties under mild conditions.

Hydrogen is considered an abundant and environmentally friendly fuel of the future.1 However, hydrogen storage remains a critical issue that hinders its application.2−5 In the past few years, various technologies, including compression, liquefaction, and metal hydriding, have been developed for hydrogen storage.6−8 Metal hydrides are promising candidates because of their safety advantage combined with their high volume-efficient storage capacity for on-board applications.5,7 Additionally, metal hydrides have excellent electrical properties.8 A large number of metal hydrides are predicted to convert into superconductors with high superconducting transition temperature at high pressure.9−11 It is worth noting that the preparation of some metal hydrides requires the reaction of a metal and hydrogen under pressure with the essential assistance of laser heating.12−14 Accordingly, finding an effective strategy to obtain metal hydrides under mild conditions is a worthwhile goal to pursue.

It is well-established that metal nanocrystals (NCs) have chemical and physical properties that differ from those of bulk metals because of their high surface-to-volume ratio and the quantum size effect. In addition, metal NCs with controllable shape and size have shown excellent performance in a variety of application areas related to catalysis, sensing, and energy storage.15−18 A few studies demonstrated that small-size metal NCs can absorb hydrogen to form metal hydrides with low hydrogen content under normal temperature and pressure conditions.19−21 Takata et al.20 found that non-hydride-forming metals in the bulk can display a hydrogen storage capability in nanostructured form because of the nanosize effects. For example, intrinsically non-hydride-forming iridium can form hydrides as a result of the decreased particle diameter of <10 nm.22 In addition, the storage capacity is improved by the increased number of defect sites because the defects may provide more entry points for hydrogen gas.23 Moreover, the defects can increase the number of active sites in the process of hydrogen dissociation, thereby accelerating hydrogenation kinetics.24 We therefore ponder whether metal NCs with more defects can easily form the corresponding metal hydrides under relatively mild conditions.

In this work, we selected rhodium (Rh) as a typical metal to study the effects of different nanostructures on the hydriding reaction. We found that Rh NCs can form rhodium monohydride (RhH) at a lower pressure than bulk Rh. The high specific surface area and structure defects of Rh NCs effectively improved the hydrogen absorption efficiency, thereby reducing the conversion pressure. Moreover, Rh NCs in the form of icosahedrons exhibited a much higher hydrogen absorption efficiency than Rh nanocubes. We further observed that much smaller irregular Rh nanoparticles are even partially converted to RhH at lower pressure as a result of the nanosize effect. Our findings open new ways of preparing metal hydrides under mild conditions.

The detailed synthetic procedures and test characterization of Rh NCs are described in the Supporting Information.
Scanning transmission electron microscopy (STEM) images clearly show that a high yield of Rh nanoicosahedrons was obtained with an average size of 13 nm (Figure 1a). A high-resolution transmission electron microscopy (HRTEM) image along the axis of an individual Rh nanoicosahedron is shown in Figure 1b. Therein, the lattice spacing of 0.22 nm on the surface of the icosahedron could be indexed to the (111) lattice plane of face-centered cubic (fcc) Rh. Actually, the icosahedron is a special crystallite form. The intrinsic icosahedron consists of 20 (111) faceted tetrahedral units with 30 twin boundaries. The twin boundaries were clearly found in all the directions, and the Rh nanoicosahedron matched well with its corresponding geometric model. The inset image shown in Figure 1b is the fast Fourier transform (FFT) of the corresponding Rh nanoicosahedron which reveals the existence of the (111) spots. The X-ray diffraction (XRD) pattern of the Rh nanoicosahedrons is shown in Figure S1, and the diffraction peaks were definitely indexed to the fcc crystal symmetry of Rh (JCPDS no. 65-2866).

We conducted high-pressure experiments with the Rh nanoicosahedrons and H2 with the assistance of a diamond anvil cell (DAC) apparatus. In situ angle-dispersive X-ray diffraction (AD-XRD) patterns of the Rh nanoicosahedrons and hydrogen system in the presence of H2 as pressure-transmitting medium (PTM).
angles when hydrogen atoms enter the lattice. It can also be seen that the reaction undergoes a process involving some hydrogen absorption steps. At the initial pressure of 1.0 GPa, the peaks of the (111) and (200) crystal plane centered at 2θ of ~16.27° and ~18.78° belong to Rh, and these Bragg peaks remain up to 3.0 GPa. With further increase of pressure to 3.5 GPa, two new diffraction peaks emerged directly and completely at a low angle position. This indicated that all the Rh was transformed into a NaCl-structure RhH. The RH formed as a result of the hydrogen atoms entering the rhodium lattice under the effect of pressure. After decompression, the recorded AD-XRD pattern showed that the samples recovered their original structure. It should be noted that the intensity of the diffraction peaks increased with the decrease of the half width, which indicated that the quenched sample has better crystallinity or grain fusion into large crystal size. Transmission electron microscopy (TEM) and HRTEM images of the sample after the release of the pressure are displayed in Figure S2. The Rh nanoicosahedrons were sintered to form large-size nanoparticles. Under the action of pressure, the compression of Rh nanoicosahedrons generated deviatoric stress across the grain boundaries of the pentagonal cyclic twinning (PCT). The deviatoric stress acts as a driving force that developed the (111) planes preferred two-dimensional nanosheets. With the increasing of pressure, the unit tetrahedrons of the icosahedron would slip along the twin boundaries under the action of the deviatoric stress. Eventually, the deviatoric stress eliminated the defects of twin boundaries, and ultimately the samples were sintered to form nanosheets.26–28

It is hard to observe hydrogen in the XRD analysis experiments because of its much lower electron density against the metal; thus, the Rietveld refinements of selected pressures of the AD-XRD patterns were recorded to confirm the crystal structure of rhodium hydrides. As presented in Figure 2a, the refinements of the AD-XRD pattern matched well with the experimental data at 3.0 GPa (Rwp = 0.43%, Rp = 0.33%). All the diffraction peaks in the profile can be readily indexed as cubic phase Rh (space group: Fm3m) with cell constants of a = 4.01 Å. At 4.0 GPa, the excellent agreement (Rwp = 0.46%, Rp = 0.34%) between the AD-XRD patterns and the experimental data at 3.0 GPa (Rwp = 0.43%, Rp = 0.33%) between the AD-XRD patterns and the experimental data at 3.0 GPa (Rwp = 0.43%, Rp = 0.33%) shows the formation of the RhH, which is consistent with the analysis of the AD-XRD patterns at selected pressures of the Rh nanocubes and H2 system.

To illustrate the bonding form of RhH, we use the Mulliken population analysis to study the Bond overlap population (BOP).29,30 The BOP is widely used to determine the ionic or covalent bonding nature of crystals. The value of the BOP indicates the degree of covalent or ionic interaction in the bond. The calculated BOP value and interatomic distances of RhH at different pressures are shown in Table 1. At 0 GPa, the BOP value of the Rh–H is 0.22eÅ, which lies between 0 and 0.5eÅ of ionic interaction, indicating its ionic character. The calculated BOP value for the Na–Cl of ionic NaCl is 0.13eÅ. With increasing pressure, the BOP value of the Rh–H is slightly reduced to 0.22eÅ. However, this value remains unchanged at 11.9 GPa. Accordingly, we can conclude that the Rh atoms and hydrogen atoms are combined in the form of ionic bonds in the pressure range from 3.5 to 11.9 GPa.

To explore the role of the structural defects in nanomaterials in hydrogenation reactions, we synthesized Rh nanocubes with dimensions similar to those of Rh nanoicosahedrons as a comparative experiment. The STEM image of Rh nanocubes revealed that the morphology of the products was uniform, with an average size of 11–12 nm (Figure 3a). The HRTEM image showed that the Rh nanocube was enclosed by (100) facets (Figure 3b). The corresponding FPT pattern confirmed that the Rh nanocube has a single crystalline structure.

<table>
<thead>
<tr>
<th>pressure (GPa)</th>
<th>bond population</th>
<th>interatomic distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.22</td>
<td>2.005</td>
</tr>
<tr>
<td>3.5</td>
<td>0.23</td>
<td>2.003</td>
</tr>
<tr>
<td>11.9</td>
<td>0.23</td>
<td>1.984</td>
</tr>
</tbody>
</table>

Table 1: Bond Overlap Population and Interatomic Distances of Rh–H as a Function of the External Pressure

Figure 3. (a and b) TEM and HRTEM images of the as-synthesized Rh nanocubes. The inset image in panel b is the FFT pattern of the corresponding Rh nanocubes. (c) Representative in situ AD-XRD patterns at selected pressures of the Rh nanocubes and H2 system.
products appeared as irregular particles with an average diameter of 5–6 nm. We further conducted high-pressure experiments under the same conditions as the previous experiments (Figure S4c). At the initial pressure of 0.2 GPa, a portion of the Rh nanoparticles was converted to RhH. The pressure is much lower than that of the Rh nanoicosahedrons and nanocubes. There are no fixed exposed planes for the Rh nanoparticles. Additionally, it reduced the effect of the different planes of Rh nanoparticles on the hydrogenation reaction. Also, the rate of hydrogenation increases as the size of the NCs decreases. However, the dramatic increase of the hydrogenation rates was not due to the small-size effect only. Defect sites have been cited as important factors in improving the kinetics of hydrogen sorption.\textsuperscript{21} For nanomaterials, the number of surface atoms increases sharply as the size of the nanostructure decreases, while the specific surface binding energy of the NCs increases rapidly. Because of the increase in the number of atoms on the surface of the NCs, the lack of atomic coordination inevitably leads to many structural defects on their surface, which makes the surface highly active and easily binds to other atoms. Therefore, a large number of defect sites formed as the particle size decreased. We thus concluded that irregular Rh nanoparticles with small size possess lower hydride transition pressure because of the combination of small-size effects and structural defects.

In general, the absorption of hydrogen during the formation of metal hydrides includes physisorption (\(\alpha\) phase) and chemisorption (\(\beta\) phase).\textsuperscript{31} Compared to bulk Rh powder, Rh nanoicosahedrons absorb hydrogen to form RhH at a much lower pressure (3.5 GPa) than the bulk Rh powder (6.1 GPa).\textsuperscript{32} This result can be explained as follows: Rh nanoicosahedrons have a large specific surface area, and the increased surface area makes the diffusion of hydrogen atoms more efficient by offering a large number of dissociation sites and allowing hydrogen atoms permeation to reach saturation quickly. Meanwhile, a nanoicosahedron is a special crystallite form. The intrinsic PCT consists of 20 (111) faceted tetrahedral units with 30 twin boundaries, in which a two-dimensional (2D) lattice expansion exists. The novel properties of metal NCs are induced by expansion due to the changes in geometry and electronic structure.\textsuperscript{33} For the hydrogenation reaction, the thermodynamics of the reaction is regarded as a key point for understanding the nanostructural effects on the properties of the metal hydrides. The Gibbs free energy (\(\Delta G\)) is the main factor to promote the hydrogenation reaction. The \(\Delta G\) in the system consists of the enthalpy of the reaction (\(\Delta H\)) and the energetic contribution due to the entropy change (\(-T\Delta S\)), and \(\Delta S\) is the entropy of formation. The change of the \(\Delta G\) is shown in the following equation: \(\Delta G = \Delta H - T\Delta S\). The enthalpy of the reaction formation of metal hydride can be affected by the properties of nanomaterials. The surface area of nanomaterials is greater than that of the corresponding bulk materials. The excess surface energy (\(E_{\text{surface}}\)) offers an excess energy for reducing the enthalpy of the formation of metal hydrides. On the other hand, the structure of the Rh nanoicosahedron is different from that of a single-crystal particle. The tetrahedral units are joined together at the (111) twin boundaries, resulting in declination defects.\textsuperscript{34} The twin boundaries induce excess energy that in turn leads to excess enthalpy. Thus, the energy (\(E_{\text{defects}}\)) offered by the grain boundary provides another tool to reduce the formation enthalpy of metal hydrides.\textsuperscript{31} The formation enthalpy of the RhH nanoicosahedron can be expressed as follows:

\[
\Delta H_{\alpha-\beta} = \Delta H_0 - E_{\text{surface}} - E_{\text{defects}}
\]

where \(\Delta H_0\) is the standard formation enthalpy of RhH. Moreover, in the process of hydrogen absorption, the unique structure of nanomaterials can affect the adsorption efficiency of hydrogen atoms. Nanomaterials provide a large number of dissociation sites due to the larger surface area and structure defects, thereby allowing fast permeation and diffusion of hydrogen atoms to the center of the material. For the Rh nanoicosahedron, besides the improved kinetics of hydrogen dissociation, the internal strain resulting from the twin boundaries of the PCT makes the binding sites of hydrogen dissociation more accessible at low pressure. Therefore, nanoicosahedron structures not only decrease the formation enthalpy of RhH but also significantly improve the absorption efficiency of hydrogen atoms.

Regarding the comparative experiment with Rh nanocubes, we eliminated the effect of the size on the reaction because of the close size of the two nanocrystals. There were no structure defects, such as grain boundaries for the Rh nanocubes. Therefore, unlike the Rh nanoicosahedrons, only the surface energy and internal stress induced by the nanostructure can affect the formation enthalpy of the Rh nanocubes and hydrogen system. Accordingly, the formation enthalpy of RhH nanocubes is summarized as follows:

\[
\Delta H_{\alpha-\beta} = \Delta H_0 - E_{\text{surface}}
\]

This made the \(\Delta H_{\alpha-\beta}\) of the Rh nanocubes larger than that of the nanoicosahedrons; thus, it required higher pressure to form RhH. Therefore, the apparent shape-dependent performance of RhH NCs, in essence, arises from the difference between their structures. When the size of the nanocrystals was sufficiently small, the surface energy of Rh nanoparticles was bigger than that of Rh nanocubes and nanoicosahedrons. Previous studies suggested that the \(\Delta H\) of the \(\alpha\) phase to \(\beta\) phase for nanoparticles decreased with decreasing particle diameter. The small \(\Delta H_{\alpha-\beta}\) indicated that the bond strength of Rh–H became weaker. This enabled Rh and hydrogen to form hydrides at low pressure. Meanwhile, Rh nanoparticles would produce structure defects during the growth process, which lead to the generation of internal strain. The effect of strain in Rh nanoparticles was mentioned above. In the process of nucleation, because of the small crystal size, fast diffusion of the hydrogen through the \(\alpha\) phase remains possible for a larger fraction of the \(\alpha-\beta\) phase transition. This can be due to the coexistence of Rh and RhH when the pressure is below 3.7 GPa. In addition, the exposed surfaces of metal NCs could affect the hydrogenation reaction properties. Pd NCs with (111) facets exhibited higher hydrogenation activity than (100) facets. In-depth research found that hydrogenation reactions can be more effectively regulated by changing the structure and size through the introduction of a high-index crystal face and more structural defects.

In summary, we utilized different structures of Rh NCs to investigate the effect of structures on the hydrogenation reaction under pressure. It was found that nanostructures can effectively improve the hydrogen absorption capacity of Rh. In addition, reducing the size of nanoparticles and introducing structural defects, such as grain boundaries, can reduce the enthalpy of metal hydrides, thereby lowering the conversion pressure of metal hydrides. These findings offer new insights into improving the hydrogen storage capacity of metal materials under mild conditions. We thus believe that it is...
possible to design materials with excellent hydrogen storage properties taking advantage of the small-size effect and structure defects, such as grain boundaries.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jpcllett.9b00216.

Details of the sample preparation and characterization, specific implementation methods for high-pressure experiments, XRD patterns, TEM and HRTEM images of pressure-induced recrystallization of Rh nanocicosahedrons, and the experimental data for small-size Rh nanoparticles (PDF)

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Notes
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